

ESSENTIAL OILS OF PLANTS FROM HISPANIOLA:
2. THE VOLATILE LEAF OIL OF *PINUS OCCIDENTALIS* (PINACEAE)*.

Thomas A. Zanoni, Robert P. Adams & Elvia Jaime Miller

Zanoni, Thomas A. (Jardín Botánico Nacional, Apartado Postal 21-9, Santo Domingo, Dominican Republic), Robert P. Adams (CSFAA, Box 7372, Baylor University, Waco, TX 79798, USA), Elvia Jaime Miller (Jardín Botánico Nacional, Apartado Postal 21-9, Santo Domingo, Dominican Republic) *Moscosa* 6: 219-222, 1990. The volatile oil from the needles of *Pinus occidentalis* Swartz (Pinaceae) was analyzed by fused silica capillary gas chromatography/ion trap mass spectroscopy (GC/ITMS). The fresh leaves yielded 0.16 g of oil/g fw. The oil was dominated by four components: β -Pinene (45.04%); Germacrene D (22.30%); α -Pinene (15.07%) and Myrcene (9.21%). All the other constituents were present in less than 1% concentrations and most were less than 0.1%. The large concentration of the sesquiterpene hydrocarbon, germacrene D, is unusual for *Pinus*.

KEY WORDS Essential oil, Monoterpenes, Sesquiterpenes, *Pinus occidentalis*, Pinaceae, Ion Trap Mass Spectroscopy.

Pinus occidentalis Swartz is the only native pine on Hispaniola. In the Dominican Republic, the pine is known as "pino", "pino de cuba", or more recently as "pino occidentalis" (to distinguish it from "pino caribea", *Pinus caribea* Morelet, which has been introduced into cultivation in the Dominican Republic and also Haiti). *Pinus occidentalis* is called "bois pin" or "bwapen" (in Creole) in Haiti. The name suggested by Little and Critchfield (1965) and Critchfield and Little (1966) - "West Indian Pine" appears to be inappropriate and probably should be referred to as "Hispaniolan pine" since it is known only from the island of Hispaniola.

The Hispaniolan pine is known from the Cordillera Central, the Sierra de Neiba, and the Sierra de Bahoruco in the Dominican Republic. For reasons unknown, it has not been seen in the Cordillera Septentrional in the northern Dominican Republic. In Haiti, it is known from the Massif du Nord, Presqu'île du Nord-Ouest, Plaine Central, Montagnes Noires, Chaîne de Matheux, Montagnes du Trou d'Eau (the western extension of the Sierra de Neiba), Massif de la Selle (the western extension of the Sierra de Bahoruco), Massif de la Hotte, and Île de la Gonave.

The pine grows from about 50 m elev. in northern Haiti (unusual occurrence) to the tops of the highest peaks on the island - Pic la Selle, Haiti (2640 m elev.) and Pico Duarte and Loma La Pelona, Dominican Republic (both about 3,075 m. elev.).

At lower elevations, from 200m (where it is normally at its lower limit) to about 800 - 1000 m, the pine occurs as a pioneer species or as an invader on land that has been burned over, abused or degraded by erosion or over-usage by man or grazing animals. The Hispaniolan pine is often mixed with broadleaved trees if the forest are left with little disturbance and if seed sources for these broadleaved species are in the vicinity. The high mountains in both countries once had extensive pine forests. At higher elevations, great expanses of pine forests may still be seen in the Dominican Republic but only small forests still exist in Haiti.

*previous article is "Essential oils from plants of Hispaniola : Part 3. The leaf oil of *Canella winterana* (Canellaceae), R. P. Adams & T. Zanoni. *J. Essential Oil Res.* 1990.

Deforestation and fires have reduced the original areas. It is thought that some stands of the pines may be maintained by natural or man-caused fires in some areas. Burning of the understory in the pine woodlands does leave the soil exposed with less organic material and facilitates the germination and survival of the seedlings if the site is not further altered by removal of vegetation or by agriculture.

Uses of the Hispaniolan pine include lumber, firewood, kindling (the resin-filled splinters are used to start cooking firewood or charcoal, being called "cuaba" in the Dominican Republic), resin for turpentine and terebintine (pine oil with kerosene, used as a cleaning agent and also as a liquid fuel for hurricane lamps in the Dominican Republic), pine oil (cleaning agent), and pino-ozua (cleaning agent, a mixture of the essential oils from the Hispaniolan pine and ozua, *Pimenta racemosa* var. *ozua* (Urb. & Ekm.) (Landrum). Occasionally it has been used as a cut-tree for Christmas and as an ornamental tree for home gardens. Only in the past 20 years or so, has it been used in reforestation on the island.

The composition of the volatile leaf oil of *P. occidentalis* has not been previously reported. As a part of our on-going research on the essential oils of plants from Hispaniola (Zanoni and Adams, 1989), the composition of the leaf oil of *P. occidentalis* is presented in this paper.

Materials and Methods

Plant materials- the samples consisted of approximately 100 g of fresh foliage (needles), from Dominican Republic: Sierra de Bahoruco, 25 km "South" of Puerto Escondido on road to Aceitillar (of Pedernales), open pine forest, elev. 1700 m. 28 August 1987. A voucher specimen (Zanoni & Pimentel 40384) is on deposit at the herbarium at the Jardín Botánico Nacional, Santo Domingo (JBSD).

The needles were kept frozen until steam distilled. They were cut into 1 cm segments and then steam distilled using a modified Clevenger apparatus (von Rudloff, 1967). Steam distillation was performed for 2 hr. and the floating oil was collected. The oil was sealed in glass vials with teflon lined caps, air mailed to RPA, and thence stored at - 20°C until analyzed.

Mass spectra were recorded with a Finnigan Ion Trap (ITD) mass spectrometer, model 800, directly couple to a Varian 6500 gas chromatograph, using a J & W DB5, 0.26 mm id x 30 m, 0.25 micron coating thickness, fused silica capillary column. The GC/ITD was operated under the following conditions: injector temperature: 220°C; transfer line: 240°C; oven temperature programmed: 60°C to 240°C @ 3°C/min; carrier gas: He @ 31.9 cm/sec or 1.017 ml/min (@ 210°C); injection size: 0.1 ul (10% soln.), split 1:20, 500 ng/on column. Tuning values for the ITD were 100, 100, 100, 100 using cedrol as a tuning standard (Adams and Edmunds, 1989; Adams, 1989). Internal standards (n-octane and n-eicosane) were added to each sample to aid in the standardization of retention times. Identifications were made by library searches of our volatile oil library, LIBR(TP) using the Finnigan library search routines based on fit (Adams, 1989). Additional searches were made of the EPA/NIH mass spectral data base (Heller and Milne, 1983, Adams, et al. 1979).

Table 1. Composition of the steam volatile leaf oil of *P. occidentalis*. Compounds are listed in order of their elution on a DB5 (= SE54) column. Data expressed as % total oil based on total ion count (TIC). Unidentified components smaller than a trace (0.05%) are not reported.

COMPOUND	% Total oil	COMPOUND	% Total oil
2-Hexanel	0.13	Thymol < metyl ether->	0.14
Tricyclene	0.06	Linalyl acetate	0.08
α -Pinene	15.07	α -Terpinenyl acetate	0.42
Camphene	0.41	PEI1, RT1378	0.08
Sabinene	0.08	Caryophyllene	0.39
β -Pinene	45.04	Bergamotene <Z- α -trans->	0.22
Myrcene	9.21	PEI2, RT1493	0.25
ρ -Cymene	0.06	α -Humulene	0.07
Limonene	0.80	Γ -Muurolene	0.17
β -Phellandrene	0.83	Germacrene D	22.30
Terpinolene	0.23	PEI3, RT1608	0.10
Linalool	0.06	α -Muurolene	0.30
Fenchol -	0.06	Γ -Cadinene	0.11
α -Campholenal	trace	δ -Cadinene	0.25
trans-Pinocarveol	0.16	PEI4, RT1888	0.44
Pinocervone	0.08	PEI5, RT1977	0.47
Borneol	trace	Torreyol	0.09
Terpin-4-ol	0.09	α -Cadinol	0.17
α -Terpineol	0.69	RT2039	0.19
Myrtenal	0.19	PEI6, RT2139	0.10

Results and Discussion

The leaf oil of *P. occidentalis* is dominated by four components (Table 1): β -pinene (45.04%); germacrene D (22.30); α -pinene (15.07) and myrcene (9.21). Although the dominance by the pinenes is common in *Pinus* (Adams and Edmunds, 1989), the presence of such a large concentration of the sesquiterpene hydrocarbon, germacrene D, appears to be unusual in the genus. Ekundayo (1978) analyzed the needle oils of *P. caribaea*, *P. elliotii*, *P. massoniana*, and *P. merkusii* and reported that the monoterpene hydrocarbons accounted for between 85 and 98% of the total oil. In a recent reexamination of the leaf oil of *P. ponderosa*, Adams and Edmunds (1989) reported that 78.7% of the total oil was composed of terpene hydrocarbons, with the largest sesquiterpene hydrocarbon being germacrene D (1.7%) and the largest concentration of an oxygenated sesquiterpene of 1.7% (nerolidol).

In addition to the "normal" kinds of terpenes and sesquiterpenes, six compounds in a chemical series of "phenyl ethyl esters" were found and are labeled as PEI1...6 in Table 1.

Several of these compounds were also found in *P. ponderosa* (Adams and Edmunds, 1989). Work is in progress on their identifications. All for the "phenyl ethyl esters" are present in small concentrations (Table 1). Their mass spectra are dominated by m/z (%) 104 (100), 43 (40-60) or 57 (60). They elute too late for phenyl ethyl acetate or phenyl ethyl propionate.

Spectral data for the unknowns: PEI1, RT1378, MW?, m/z (%) 104 (100), 43(99), 41(33), 78(22), 91(19), 51(13), 67(12), 57(7), 147(2), 119(1), 133(1); PEI2, RT1493, MW?, m/z (%) 104(100), 43(66), 71(23), 41(20), 78(18), 91(13), 65(11), 51(8); PEI3, RT1608, MW?, m/z (%) 104(100), 57(60), 41(28), 91(17), 78(15), 51(9), 65(8), 119(1), 133(1), 161(1); PEI4, RT1888, MW? m/z (%), 104(100), 43(38), 41(21), 81(19), 78(12), 91(10), 65(8), 51(6), 55(6), 71(4); PEI5, RT1977, MW? m/z (%) 104(100), 43(45), 41(22), 71(12), 91(12), 79(11), 55(6), 65(6), 161(4), 121(1), 133(1); PEI6, RT2139, MW?, m/z (%) 104(100), 43(25), 41(20), 95(17), 77(10), 57(9), 91(9), 121(1), 135(1); RT2039, C150H?, m/z (%) 41(100), 79(77), 93(69), 67(50), 55(44), 107(32), 121 (28), 136(20), 163(18), 149(10), 207(10), 191(6).

Acknowledgments

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